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(54) **Process of producing hydroxyalkanal**

Verfahren zur Herstellung von Hydroxyaldehyden

Procédé pour la production d'hydroxyaldéhydes

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EP-A- 0 487 903 **US-A- 3 536 763**

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Description

[0001] The present invention relates to a process of producing hydroxyalkanal by hydrating an unsaturated aldehyde with a solution in the presence of a catalyst.

5 [0002] In conventional processes, an unsaturated aldehyde, namely, acrolein, is hydrated with a solution in the presence of a catalyst to obtain hydroxyalkanal, namely, 3-hydroxypropanal(3-hydroxypropionaldehyde), which will be explained in the following paragraphs.

[0003] U.S. Patent No. 2,434,110 discloses a process, in which a mineral acid, such as a sulfuric acid, is used as a homogeneous acid catalyst for the above reaction step. However, 3-hydroxypropanal retains low selectivity in this process, and thus is not produced efficiently. In addition, neither 3-hydroxypropanal is readily separated from the homogeneous catalyst, nor the catalyst can be re-used easily.

10 [0004] To eliminate such a drawback, processes for improving the selectivity of 3-hydroxypropanal are proposed in the undermentioned publications. U.S. Patent No. 3,536,763 discloses a process, in which an acid ion exchange resin is used as a heterogeneous acid catalyst for the above reaction step. U.S. Patent No. 5,015,789 and U.S. Patent No. 15 5,171,898 disclose processes, in which an ion exchange resin containing a phosphonate group, an amino group, or an aminophosphate group is used as a heterogeneous acid catalyst for the above reaction step. U.S. Patent No. 5,093,537 discloses a process, in which alumina bonding zeolite is used as a heterogeneous acid catalyst for the above reaction step. U.S. Patent No. 5,276,201 discloses a process, in which TiO_2 carrying a phosphoric acid is used as a heterogeneous acid catalyst for the above reaction step. Also, U.S. Patent No. 5,284,979 discloses a process, in which the above reaction step is performed using a buffer solution containing a carboxylic acid and tertiary amine in the presence of an acid catalyst.

[0005] If a resulting solution of the raw material, acrolein, has low density (i.e., lower than 20 percent by weight), 3-hydroxypropanal retains satisfactory selectivity, thereby making it possible to obtain 3-hydroxypropanal at high selectivity by the above processes.

25 [0006] However, the inventors of the present invention found that when an industrially advantageous high-density acrolein solution (i.e., 20 or more percent by weight) is used for the reaction in each of the above processes, a reaction product, 3-hydroxypropanal, triggers an active consecutive reaction (side reaction) because it has an aldehyde group. In other words, the above processes have a drawback that the selectivity from acrolein to 3-hydroxypropanal, and hence the selectivity of 3-hydroxypropanal is reduced as the density of the solution increases.

30 [0007] In addition, the heterogeneous acid catalysts used in the above conventional processes have poor resistance to heat. Thus, if a reaction temperature is raised (over 65°C) to accelerate the hydration reaction, the heterogeneous acid catalysts are deactivated, thereby reducing the selectivity of 3-hydroxypropanal. Further, although the reason why is not apparent, the metal-carrying heterogeneous acid catalysts used in the above conventional processes retain a low reaction rate in hydration, thereby reducing an industrially advantageous short-time conversion of acrolein.

35 [0008] Therefore, these processes are not industrially satisfactory, because not only the conversion of acrolein is low, but also the reaction rate can not be increased by heating, besides the yield of 3-hydroxypropanal can not be improved by increasing the density of acrolein solution.

[0009] It is therefore an object of the present invention to provide a process of producing hydroxyalkanal capable of (1) increasing a reaction rate by heating while improving an industrially advantageous short-time conversion of an unsaturated aldehyde with the use of a heat-resistant catalyst, and (2) producing hydroxyalkanal at high yield and selectivity out of an industrially advantageous high-density unsaturated aldehyde solution.

40 [0010] To fulfill the above object, the inventors of the present invention performed experiments of processes for producing hydroxyalkanal by hydrating an unsaturated aldehyde with a solution in the presence of a catalyst, and found that the selectivity from an unsaturated aldehyde to hydroxyalkanal and the yield of hydroxyalkanal were improved when the catalyst was a carboxylic-acid-based resin having a substitutional group of a specific structure, and/or a carboxylic-acid-based resin made of a copolymer of an unsaturated monomer (A) containing a carboxyl group with an unsaturated monomer (B) containing an amide group or both amide and amino groups. It was also acknowledged that the carboxylic-acid-based resin serving as the catalyst retained excellent heat resistance and the reaction temperature could be raised, thereby making it possible to increase the reaction rate by heating. In other words, the gist of the present invention is to use a heat-resistant carboxylic-acid-based resin as a catalyst, and the effects are that (1) the reaction rate can be raised by heating, and (2) hydroxyalkanal can be produced at high selectivity and yield out of an industrially advantageous high-density unsaturated aldehyde solution.

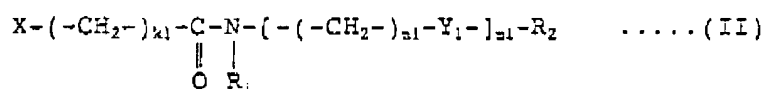
45 [0011] The inventors of the present invention also found that the reaction rate of the hydration was increased and the selectivity from an unsaturated aldehyde to hydroxyalkanal and the yield of hydroxyalkanal were also improved when the catalyst was a metal-carrying ion exchange resin. In other words, the gist of the present invention is to use a metal-carrying ion exchange resin as a catalyst, and the effects are that (1) an industrially advantageous short-time conversion of an unsaturated aldehyde is improved, and (2) hydroxyalkanal can be produced at high selectivity and yield out of an industrially advantageous high-density unsaturated aldehyde solution.

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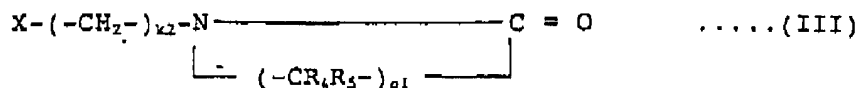
[0012] To fulfill the above object, a process of producing hydroxyalkanal in accordance with the present invention is characterized by comprising a step of hydrating an unsaturated aldehyde expressed by Formula (I) below with a solution in the presence of a carboxylic-acid-based resin containing a substitutional group having at least one structure selected from a group consisting of structures expressed by Formulas (II), (III), (IV) below:



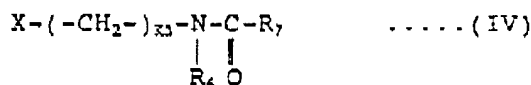
where R represents a hydrogen atom or hydrocarbon group having up to five carbons;



where R_i and R₂ respectively represent a hydrogen atom, hydrocarbon group having up to five carbons, or $\text{-(CH}_2\text{)}_{p_1}\text{-X}$ group, p₁, k₁, and m₁ respectively represent an integer from zero to six, n₁ represents an integer from one to six, Y₁ represents -O-, -S-, or -NR₃-, R₃ represents a hydrogen atom or hydrocarbon group having up to five carbons, and X represents a carboxylic-acid-based resin main body;



where R₄ and R₅ respectively represent a hydrogen atom or hydrocarbon group having up to five carbons, k₂ represents an integer from zero to six, q₁ represents an integer from three to six, and X represents a carboxylic-acid-based resin main body;



where R₆ represents a hydrogen atom, hydrocarbon group having up to five carbons, or $\text{-(CH}_2\text{)}_{p_2}\text{-X}$ group, p₂ represents an integer from zero to six, R₇ represents a hydrocarbon group having up to five carbons or $\text{-(CH}_2\text{)}_{p_3}\text{-X}$ group, p₃ and k₃ respectively represent an integer from zero to six, and X represents a carboxylic-acid-based resin main body.

[0013] According to the above process, not only a reaction rate can be increased by heating, but also the consecutive reaction (side reaction) of the reaction product, namely, hydroxyalkanal, is curbed, thereby making it possible to produce hydroxyalkanal at high selectivity and yield out of a high-density unsaturated aldehyde solution. That is to say, using a heat-resistant carboxylic-acid-based resin can increase the reaction rate by heating and trigger a reaction of an industrially advantageous high-density unsaturated aldehyde solution, thereby improving the yield of hydroxyalkanal.

[0014] To fulfill the above object, a process of producing hydroxyalkanal in accordance with the present invention is characterized by comprising a step of hydrating an unsaturated aldehyde expressed by Formula (I) with a solution in the presence of a carboxylic acid based resin as described above but which is a metal-carrying ion exchange resin.

[0015] According to the above process, not only a reaction rate can be increased, but also the consecutive reaction

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(side reaction) of the reaction product, namely, hydroxyalkanal, is curbed, thereby making it possible to produce hydroxyalkanal at high selectivity and yield out of a high-density unsaturated aldehyde solution. That is to say, using a metal-carrying ion exchange resin can improve an industrially advantageous short-time conversion of an unsaturated aldehyde, and trigger a reaction of a high-density unsaturated aldehyde solution, thereby improving the yield of hydroxyalkanal.

[0016] Other objects and advantages of the present invention will become apparent from the detailed description to follow taken in conjunction with the appended claims.

[0017] The raw material of the present invention, namely, an unsaturated aldehyde (2-alkenal) expressed by Formula (I) mentioned above, is not especially limited. In Formula (I), however, a substitutional group represented by R is a hydrogen atom or hydrocarbon group having up to five carbons, and the hydrocarbon group referred herein is a methyl group, ethyl group, propyl group, butyl group, or amyl group. Examples of the unsaturated aldehyde are: acrolein, methacrolein, 2-formyl-1-butene, 2-formyl-1-pentene, 2-formyl-1-hexene, 2-formyl-1-heptene, and the like. Of all these examples, a preferable unsaturated aldehyde is acrolein.

[0018] According to the process in accordance with the present invention, either 2-hydroxyalkanal or 3-hydroxyalkanal is selectively obtained from these examples. More precisely, in case of acrolein whose substitutional group represented by R in Formula (I) is a hydrogen atom, 3-hydroxyalkanal, namely, 3-hydroxypropanal (3-hydroxypropionaldehyde) is selectively obtained. In case of an unsaturated aldehyde whose substitutional group represented by R in Formula (I) is a hydrocarbon group, 2-hydroxyalkanal is selectively obtained. Note that 3-hydroxypropanal, obtained when acrolein is used as the unsaturated aldehyde, is an industrially important raw material of 1,3-propanediol.

[0019] The density of an unsaturated aldehyde solution (hereinafter referred to as the density) is, although it depends on unsaturated aldehyde's solubility to water, a reaction temperature, etc., preferably in a range between 5 percent by weight and saturation, more preferably in a range between 5 percent by weight and 50 percent by weight, further preferably in a range between 20 percent by weight and 50 percent by weight, and most preferably in a range between 25 percent by weight and 40 percent by weight. The density lower than 5 percent by weight is not preferable because the yield of hydroxyalkanal is reduced. The density exceeding the saturation is not preferable either because an undissolved unsaturated aldehyde triggers a polymerization reaction or the like, and thus reduces the selectivity to hydroxyalkanal.

[0020] The catalyst used in the present invention may be

(1) a carboxylic-acid-based resin containing a substitutional group having at least one structure selected from a group consisting of structures represented by Formulas (II), (III), (IV) mentioned above;

(2) a carboxylic-acid-based resin as described in (1) above which is made of a copolymer of an unsaturated monomer (A) containing a carboxyl group with an unsaturated monomer (B) containing an amide group or both an amide and amino group; or

(3) a carboxylic acid based resin according to (1) or (2) above which is a metal-carrying ion exchange resin.

[0021] In short, the catalyst used in the present invention is (1) a carboxylic-acid-based resin containing a substitutional group having at least one structure selected from a group consisting of structures expressed by Formulas (II) through (IV), (2) a carboxylic-acid-based resin made of a copolymer of the unsaturated monomer (A) with the unsaturated monomer (B), or (3) a metal-carrying ion exchange resin. One or more than one of these catalysts are used. Note that in Formulas, X represents a carboxylic-acid-based resin main body, and a carboxylic-acid-based resin is a polymer containing a number of free carboxyl groups. Also, a hydrocarbon group having up to five carbons referred in Formulas (II) through (IV) is a methyl group, ethyl group, propyl group, butyl group, or amyl group.

[0022] A carboxylic-acid-based resin containing an amide group (substitutional group) having a structure expressed by Formula (II), (III), or (IV) is not especially limited. The carboxylic-acid-based resin main body may be a homopolymer of monomers (hereinafter referred to as comonomer for the explanation's convenience) containing a carboxyl group or a copolymer of a monomer containing a carboxyl group with another polymer which can copolymerize with the aforementioned monomer containing a carboxyl group.

[0023] The monomer containing a carboxyl group includes, but is not limited to, a carboxylic acid, such as a (meta) acrylic acid, a maleic acid, and a fumaric acid. One or more than one of these monomers are used as occasion demands.

[0024] The comonomer may be, but is not limited to, a monomer including an olefin group. Examples of the comonomer are: ester of the above-mentioned monomer containing a carboxyl group, styrene, vinylpyridine. The comonomer may also contain a function group other than the carboxyl group, such as a phosphate group, a sulfonate group, hydroxyl group. One or more than one of these comonomers are used.

[0025] Of all the carboxylic-acid-based resins including an amide group having a structure expressed by Formula (II), a carboxylic-acid-based resin whose bivalent substitutional group represented by Y₁ includes either a nitrogen atom or sulfur atom is preferable, and the one whose Y₁ includes a sulfur atom is particularly preferable in terms of catalytic reactivity. Also, of all the carboxylic-acid-based resins including an amide group having a structure expressed

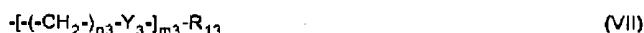
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by Formula (III), a carboxylic-acid-based resin having an amide group represented by q, whose cyclic unit is three is preferable in terms of catalytic reactivity.

[0026] A preferred carboxylic-acid-based resin (main body) is a (meta)acrylic-acid-based resin, and when the (meta)acrylic-acid-based resin includes an amide group, a (meta)acrylic acid-(meta)acrylamides copolymer and a (meta)acrylic acid-vinylpyrrolidones polymer are preferable. The (meta)acrylic acid-(meta)acrylamides copolymer includes, but is not limited to, a (meta)acrylic acid-(meta)acrylamide copolymer, a (meta)acrylic acid-N,N-dimethyl(meta)acrylamide copolymer, a (meta)acrylic acid-N-isopropyl(meta)acrylamide copolymer, a (meta)acrylic acid-N,N-dimethylaminopropyl(meta)acrylamide copolymer. The (meta)acrylic acid-vinylpyrrolidones polymer includes, but is not limited to, an acrylic acid-N-vinylpyrrolidones copolymer.

[0027] The carboxylic-acid-based resin made of a copolymer of the unsaturated monomer (A) with the unsaturated monomer (B) is not especially limited. The unsaturated monomer (A) includes, but is not limited to, the above-mentioned monomer containing a carboxyl group.

[0028] A substitutional group expressed by Formula (VII) below may bond to a nitrogen atom composing the amide group or either the amide or amino group of the unsaturated monomer (B).



where n_3 represents an integer from one to six, Y_3 represents --O-- , --S-- , $\text{--NR}_{14}\text{--}$, or $\text{--CH}_2\text{--}$, R_{14} represents a hydrogen atom or hydrocarbon having up to five carbons, m_3 represents an integer from zero to six, R_{13} , when $m_3 \neq 0$, represents a hydrogen atom, hydrocarbon group having up to five carbons, or Brønsted acid residue and, when $m_3 = 0$, a hydrogen atom or hydrocarbon group having up to five carbons. Further, a carboxylic-acid-based resin may be a copolymer of the unsaturated monomer (A) with the unsaturated monomer (B) and the above-mentioned comonomer. Note that a Brønsted acid residue referred in Formula (VII) is a group liberating a proton such as a carboxyl group, phosphate group, a phosphite group, sulfonate group, and hydroxyl group. Note that the Brønsted acid residue group referred in the present invention includes a hydrocarbon group having up to five carbons and at least one hydrogen atom substituted by the above group liberating a proton.

[0029] One or more than one of these carboxylic-acid-based resins are used as occasion demands. Note that a process of producing the carboxylic-acid-based resin is not especially limited.

[0030] Although it depends on the kinds of the unsaturated aldehyde, reaction conditions, etc., the ratio of the number of nitrogen containing groups and the number of carboxyl groups of a carboxylic-acid-based resin (the number of the nitrogen containing groups/the number of carboxyl groups) is preferably in a range between 1/1000 and 1/1, more preferably in a range between 1/100 and 1/1.5(2/3), and most preferably in a range between 1/20 and 1/2. The nitrogen containing group referred herein is an amide group having a structure expressed by Formula (II), (III), or (IV) or amide group residue derived from the unsaturated monomer (3). Neither a ratio smaller than 1/1000 nor a ratio greater than 1/1 is preferable, because the consecutive reaction (side reaction) of the reaction product, namely, hydroxyalkanal, can not be curbed.

[0031] When the carboxylic-acid-based resin is a (meta)acrylic acid-(meta)acrylamides copolymer, an amount of (meta)acrylamide in the copolymer is determined in a range between 0.1 percent by mole and 50 percent by mole depending on the kinds of the unsaturated aldehyde, reaction conditions, etc. Further, when the carboxylic-acid-based resin is a (meta)acrylic acid-vinylpyrrolidones copolymer, an amount of a vinylpyrrolidone in the copolymer is determined in a range between 0.1 percent by mole and 50 percent by mole depending on the kinds of the unsaturated aldehyde, reaction conditions.

[0032] A metal-carrying carboxylic-acid-based resin is preferable to obtain hydroxyalkanal at high selectivity and yield. Metal referred herein includes copper, lead, nickel, zinc, iron, cobalt, bismuth, tin, antimony, alkaline earth metal. Of all these examples, copper, and in particular, lead are preferable because hydroxyalkanal can be produced at high selectivity and yield.

[0033] Although it depends on the composition of a carboxylic-acid-based resin, an amount of metal carried by the carboxylic-acid-based resin is preferably in a range between 0.001 percent by weight and 10 percent by weight, and more preferably in a range between 0.01 percent by weight and 5 percent by weight, and most preferably in a range between 0.01 percent by weight and 1 percent by weight. A metal carrying amount less than 0.001 percent by weight is not preferable because it is insufficient to realize the effect of having the metal be carried by the resin. A metal carrying amount exceeding 10 percent by weight is not preferable either because the yield of hydroxyalkanal is reduced. Note that "carrying" referred herein does not specify a particular form, in other words, either a salt or chelate and either an adsorption type or inclusion type will do. Also, either metal ions or metal will do. Examples of metal ions are an oxide, a halide, a sulfide.

[0034] A process of having the metal be carried by a carboxylic-acid-based resin is not especially limited, and any

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known method is applicable. For example, when lead is to be carried by a carboxylic-acid-based resin, the carboxylic-acid-based resin is soaked in a solution of a predetermined amount of lead compounds, such as a lead nitrate or lead acetate, and stirred under predetermined conditions to perform a cation exchange. Subsequently, the carboxylic-acid-based resin is collected by filtration or the like and rinsed with water.

[0035] The carboxylic-acid-based resin thus obtained is not necessarily dissolved uniformly in an unsaturated aldehyde solution, and the state of the carboxylic-acid-based resin in the unsaturated aldehyde is not especially limited; however, a solid carboxylic-acid-based resin is preferred. A crosslinking agent may be used in producing the carboxylic-acid-based resin, and neither an adding amount nor the kind thereof is especially limited.

[0036] The reason why a metal-carrying carboxylic-acid-based resin exhibits an excellent catalytic action in producing hydroxyalkanal out of an unsaturated aldehyde is not apparent, but the metal-carrying carboxylic-acid-based resin is assumed to curb the consecutive reaction of the reaction product, namely, hydroxyalkanal.

[0037] In case that the unsaturated aldehyde is acrolein, it is preferable to add 1,3-propanediol, which is derived from the object product, namely, 3-hydroxypropanal, to the reaction solution to obtain 3-hydroxypropanal at high selectivity and yield. An adding amount of 1,3-propanediol with respect to acrolein is preferably in a range between 0.001 percent by weight and 10 percent by weight, more preferably in a range between 0.01 percent by weight and 5 percent by weight, further preferably in a range between 0.1 percent by weight and 2 percent by weight, and most preferably about 1 percent by weight. An adding amount less than 0.001 percent by weight is not preferable because it is insufficient to realize the effect of adding 1,3-propanediol. An adding amount exceeding 10 percent by weight is not preferable either because the yield of 3-hydroxypropanal is reduced.

[0038] The reason why adding 1,3-propanediol to the reaction solution brings excellent action and effect in producing 3-hydroxypropanal out of acrolein is not apparent, but 1,3-propanediol is assumed to bond to a carboxylic-acid-based resin where the reaction takes place, so that the bonded portion will be masked to some extent, thereby curbing the consecutive reaction of the reaction product, namely, 3-hydroxypropanal.

[0039] A metal-carrying ion exchange resin is not especially limited. Any ion exchange resin which is suitable for the hydration reaction of an unsaturated aldehyde will do. Metal carried by the ion exchange resin is not especially limited either, but preferred metal is lead. An amount of the ion exchange resin with respect to the unsaturated aldehyde is not especially limited, and it can be determined depending on the kinds of the unsaturated aldehyde and ion exchange resin. A process of producing the ion exchange resin is not especially limited.

[0040] Although it depends on the composition of an ion exchange resin, an amount of metal carried by the ion exchange resin is preferably in a range between 0.001 percent by weight and 10 percent by weight, more preferably in a range between 0.01 percent by weight and 5 percent by weight, and most preferably in a range between 0.01 percent by weight and 1 percent by weight. A metal-carrying amount less than 0.001 percent by weight is not preferable because it is insufficient to realize the effect of having the metal be carried by the ion exchange resin. A metal-carrying amount exceeding 10 percent by weight is not preferable either because the yield of hydroxyalkanal is reduced.

[0041] A process of having the metal be carried by an ion exchange resin is not especially limited, and it can be done in the same manner as the metal-carrying carboxylic-acid-based resin.

[0042] The carboxylic acid added to the reaction solution in the present invention as occasion demands is not especially limited, and either a monocarboxylic acid or polycarboxylic acid will do. Examples of the carboxylic acid are: (1) a monocarboxylic acid, such as a formic acid, an acetic acid, a (meta)acrylic acid, and (2) a dicarboxylic acid, such as an oxalic acid. Of all these examples, a polycarboxylic acid, in particular, a dicarboxylic acid, such as oxalic acid, is preferable.

[0043] An adding amount of the carboxylic acid to the reaction solution with respect to the unsaturated aldehyde is, although it depends on the kinds of the unsaturated aldehyde and carboxylic acid, etc., preferably in a range between 0.01 percent by weight and 10 percent by weight, more preferably in a range between 0.01 percent by weight and 5 percent by weight, and most preferably in a range between 0.01 percent by weight and 3 percent by weight. An adding amount less than 0.01 percent by weight is not preferable because it is not sufficient to realize the effect of adding the carboxylic acid. An adding amount exceeding 10 percent by weight is not preferable either because the yield of hydroxyalkanal is reduced.

[0044] A reaction temperature at which an unsaturated aldehyde is hydrated using a catalyst is not especially limited, but a preferable range is between 50°C and 250°C. In case that acrolein is used as the unsaturated aldehyde, a preferable range is between 50°C and 140°C. A reaction temperature below 50°C is not economically preferable because a reaction rate is decreased and a hydration reaction takes a long time. A reaction temperature exceeding 250°C is not preferable either because the unsaturated aldehyde triggers a side reaction, such as polymerization, and thus reduces the yield of hydroxyalkanal.

[0045] The present invention can be performed in a batch, semi-batch, or continuous manner, but in any case, a closed vessel is preferred for the reaction step. A reaction pressure inside the closed vessel is not especially limited, but a preferable range is between 0.1 MPa and 2 MPa. In case that a reaction takes place below a boiling point of the unsaturated aldehyde, it is preferable to apply a reaction pressure in a range between 0.1 MPa and 0.5 MPa to the

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reaction vessel by taking a vaporization pressure of the unsaturated aldehyde and other ingredients into consideration. The above reaction pressure is applied, for example, by filling an inert gas (N₂ gas, He gas, etc.) into the reaction vessel. The higher the reaction pressure, the more the unsaturated aldehyde dissolves in water and the higher the yield of hydroxyalkanal becomes. On the other hand, the anti-pressure structure of the reaction vessel must be reinforced, which increases the size of the vessel undesirably. Thus, when setting a reaction pressure, these factors must be taken into consideration.

[0046] When the reaction ends, the object product, namely, a hydroxyalkanal solution, can be readily obtained by a simple separation process, such as filtration and distillation. Further, hydroxyalkanal can be readily separated from the solution if so desired. In case of 3-hydroxyalkanal of hydroxyalkanals, it may exist in the form of a hemiacetal and an acetal in the solution, but they can be easily converted into 3-hydroxyalkanal. Likewise, hydroxyalkanal, in the presence of alcohol, may exist in the form of a hemiacetal and an acetal of the corresponding alcohol, but they can be easily converted into hydroxyalkanal.

[0047] Note that collected water, carboxylic-acid-based resin and ion exchange resin serving as a catalyst, carboxylic acid, and unreacted unsaturated aldehyde can be used repetitively for the hydration reaction.

[0048] Hereinafter, the present invention is illustrated by the following examples of a preferred embodiment in comparison with comparative examples not according to the invention. However, the present invention is not limited to the undermentioned examples. Note that a conversion of the unsaturated aldehyde expressed by Formula (I) and the selectivity of the resulting hydroxyalkanal are defined as follows:

(1) A conversion of unsaturated aldehyde(%) = (the mole number of consumed unsaturated aldehyde/the mole number of supplied unsaturated aldehyde) × 100

(2) Selectivity of hydroxyalkanal(%) = (the mole number of unsaturated aldehyde converted into hydroxyalkanal/the mole number of consumed unsaturated aldehyde) × 100

(3) Selectivity of dimerized hydroxyalkanal (%) = (the mole number of unsaturated aldehyde converted into dimerized hydroxyalkanal /the mole number of consumed unsaturated aldehyde) × 100.

[0049] The amounts of the unsaturated aldehyde, hydroxyalkanal, and dimerized hydroxyalkanal are measured in any known manner, and gas chromatography (GC), one of known methods, is used in the present invention.

[FIRST EXAMPLE]

[0050] A predetermined amount of water is poured into a reaction vessel equipped with a thermometer, a stirring instrument, and the like, and a predetermined amount of an unsaturated aldehyde, namely, acrolein, is also poured into the reaction vessel, so that the density of the resulting solution is 17 percent by weight. Next, a predetermined amount of a catalyst, namely, acrylic acid-acrylamide copolymer (carboxylic-acid-based resin), is added to the solution. The amount of acrylamide in the acrylic acid-acrylamide copolymer is 5 percent by mole. The above reaction solution is subject to reaction for three hours with stirring at 80°C to hydrate acrolein. The reaction conditions are set forth in TABLE 1 below.

[0051] When the reaction ends, the resulting reaction solution is filtered, and analyzed in a predetermined manner, the results of which are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 44%
- (2) selectivity of 3-hydroxypropanal : 57%
- (3) selectivity of dimerized 3-hydroxypropanal: 9%
- (4) selectivity of hydroxyalkanal : 66%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[0052] There is produced a solution containing 8.1 percent by weight of 3-hydroxypropanal and 1.3 percent by weight of dimerized 3-hydroxypropanal both obtained as the result of the above hydration reaction. A known raney nickel

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catalyst is added to the resulting solution to hydrogenate 3-hydroxypropanal and dimerized 3-hydroxypropanal. Reaction conditions are: a hydrogen pressure of 10 MPa, a reaction temperature of 60°C, and reaction time of six hours. When the reaction ends, the resulting solution is analyzed and it is acknowledged that there is produced 1,3-propanediol in an amount equal to a total of 3-hydroxypropanal and dimerized 3-hydroxypropanal. In other words, 1,3-propanediol is quantitatively produced. This indicates that dimerized 3-hydroxypropanal is converted into 1,3-propanediol by a known hydrogenation process.

[SECOND EXAMPLE]

[0053] An analysis is conducted in the same manner as the first example except that lead is carried by acrylic acid-acrylamide copolymer serving as the catalyst, 2.5 percent by weight of 1,3-propanediol with respect to acrolein is added to the reaction solution, and the reaction temperature is increased to 90°C. An amount of lead carried by the acrylic acid-acrylamide copolymer is kept equal to or lower than a predetermined level, namely, not more than 5 percent by weight. The reaction conditions are set forth in TABLE 1 below.

[0054] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 51%
- (2) selectivity of 3-hydroxypropanal : 77%
- (3) selectivity of dimerized 3-hydroxypropanal: 15%
- (4) selectivity of hydroxyalkanal : 92%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[THIRD EXAMPLE]

[0055] An analysis is conducted in the same manner as the second example except that the density of acrolein is increased to 28 percent by weight from 17 percent by weight. The reaction conditions are set forth in TABLE 1 below.

[0056] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 38%
- (2) selectivity of 3-hydroxypropanal : 64%
- (3) selectivity of dimerized 3-hydroxypropanal: 23%
- (4) selectivity of hydroxyalkanal : 87% (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[FOURTH EXAMPLE]

[0057] An analysis is conducted in the same manner as the third example except that the amount of acrylamide in the acrylic acid-acrylamide copolymer is increased to 20 percent by mole from 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

[0058] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 56%
- (2) selectivity of 3-hydroxypropanal : 67%
- (3) selectivity of dimerized 3-hydroxypropanal: 12%
- (4) selectivity of hydroxyalkanal : 79%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[FIFTH EXAMPLE]

[0059] An analysis is conducted in the same manner as the third example except that acrylic acid-N,N-dimethylacrylamide copolymer is used instead of acrylic acid-acrylamide copolymer. The amount of N,N-dimethylacrylamide acid-N,N-dimethylacrylamide in the acrylic copolymer is 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

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[0060] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 41%
- (2) selectivity of 3-hydroxypropanal : 60%
- (3) selectivity of dimerized 3-hydroxypropanal: 20%
- (4) selectivity of hydroxyalkanal : 80%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[SIXTH EXAMPLE]

[0061] An analysis is conducted in the same manner as the third example except that acrylic acid-N-isopropylacrylamide copolymer is used instead of acrylic acid-acrylamide copolymer. The amount of N-isopropylacrylamide in the acrylic acid-N-isopropylacrylamide copolymer is 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

[0062] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 42%
- (2) selectivity of 3-hydroxypropanal : 57%
- (3) selectivity of dimerized 3-hydroxypropanal: 19%
- (4) selectivity of hydroxyalkanal : 76%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[SEVENTH EXAMPLE]

[0063] An analysis is conducted in the same manner as the third example except that acrylic acid-N,N-dimethylaminopropylacrylamide copolymer is used instead of acrylic acid-acrylamide copolymer. The amount of N,N-dimethylaminopropylacrylamide in the acrylic acid-N,N-dimethylaminopropylacrylamide copolymer is 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

[0064] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 46%
- (2) selectivity of 3-hydroxypropanal : 57%
- (3) selectivity of dimerized 3-hydroxypropanal: 18%
- (4) selectivity of hydroxyalkanal : 75%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[EIGHTH EXAMPLE]

[0065] An analysis is conducted in the same manner as the third example except that acrylic acid-N,N-diethylacrylamide copolymer is used instead of acrylic acid-acrylamide copolymer. The amount of N,N-diethylacrylamide in the acrylic acid-N,N-diethylacrylamide copolymer is 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

[0066] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 58%
- (2) selectivity of 3-hydroxypropanal : 65%
- (3) selectivity of dimerized 3-hydroxypropanal: 12%
- (4) selectivity of hydroxyalkanal : 77%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

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[NINTH EXAMPLE]

[0067] An analysis is conducted in the same manner as the first example except that acrylic acid-N,N-dimethylaminopropylacrylamide copolymer is used instead of acrylic acid-acrylamide copolymer, 1.3 percent by weight of 1,3-propanediol with respect to acrolein is added to the reaction solution, and a reaction temperature is increased to 90°C. The amount of N,N-dimethylaminopropylacrylamide in the acrylic acid-N,N-dimethylaminopropylacrylamide copolymer is 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

[0068] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 30%
- (2) selectivity of 3-hydroxypropanal : 64%
- (3) selectivity of dimerized 3-hydroxypropanal: 16%
- (4) selectivity of hydroxyalkanal : 80%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[TENTH EXAMPLE]

[0069] An analysis is conducted in the same manner as the first example except that acrylic acid-N-vinylpyrrolidone copolymer is used instead of acrylic acid-acrylamide copolymer, and 2.5 percent by weight of 1,3-propanediol with respect to acrolein is added to the reaction solution. The amount of N-vinylpyrrolidone in the acrylic acid-N-vinylpyrrolidone copolymer is 5 percent by mole. The reaction conditions are set forth in TABLE 1 below.

[0070] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 28%
- (2) selectivity of 3-hydroxypropanal : 71%
- (3) selectivity of dimerized 3-hydroxypropanal: 8%
- (4) selectivity of hydroxyalkanal : 79%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[ELEVENTH EXAMPLE]

[0071] An analysis is conducted in the same manner as the tenth example except that the density of acrolein is increased to 28 percent by weight from 17 percent by weight. The reaction conditions are set forth in TABLE 1 below.

[0072] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 17%
- (2) selectivity of 3-hydroxypropanal : 65%
- (3) selectivity of dimerized 3-hydroxypropanal: 9%
- (4) selectivity of hydroxyalkanal : 74%
- (total of (3) and (4))

The catalyst used herein renders excellent heat resistance and can be used repetitively for the hydration reaction.

[FIRST COMPARATIVE EXAMPLE]

[0073] An analysis is conducted in the same manner as the second example except that an aluminum-carrying ion exchange resin is used instead of the lead-carrying acrylic acid-acrylamide copolymer, the reaction temperature is lowered to 70°C, and no 1,3-propanediol is added to the reaction solution. Duolite C467, namely, "Duolite" of Rohm & Haas Co., is used as the ion exchange resin, and an amount of lead carried by the resin is kept equal to or lower than a predetermined level, namely, not more than 5 percent by weight. The reaction conditions are set forth in TABLE 1 below.

[0074] The results of the analysis are set forth below and TABLE 2 below.

- (1) conversion of acrolein : 44%

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- (2) selectivity of 3-hydroxypropanal : 46%
 (3) selectivity of dimerized 3-hydroxypropanal: 5%
 (4) selectivity of hydroxyalkanal : 51%
 (total of (3) and (4))

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The catalyst used herein renders poor heat resistance and can not be used repetitively for the hydration reaction.

TABLE 1

	ACROLEIN DENSITY (%WT)	CARBOXYLIC-ACID- BASED RESIN (COPOLYMER)	TEMP. (°C)	TIME (HR)	1,3-PROPANE -DIOL (%WT)	AMOUNT OF Pb (%WT)
EX. 1	17	A-ACRYLAMIDE (ACRYLAMIDE 5%MOL)	80	3	---	--
EX. 2	17	A-ACRYLAMIDE (ACRYLAMIDE 5%MOL)	90	3	2.5	5 OR LESS
EX. 3	28	A-ACRYLAMIDE (ACRYLAMIDE 5%MOL)	90	3	2.5	5 OR LESS
EX. 4	28	A-ACRYLAMIDE (ACRYLAMIDE 20%MOL)	90	3	2.5	5 OR LESS
EX. 5	28	A-N,N-DIMETHYL ACRYLAMIDE (N,N- DIMETHYL ACRYLAMIDE 5%MOL)	90	3	2.5	5 OR LESS
EX. 6	28	A-N-ISOPROPYL ACRYLAMIDE (N- ISOPROPYL- ACRYLAMIDE 5%MOL)	90	3	2.5	5 OR LESS
EX. 7	28	A-N,N-DIMETHYL AMINOPROPYL ACRYLAMIDE (N,N- DIMETHYL AMINO- PROPYLACRYLAMIDE 5%MOL)	90	3	2.5	5 OR LESS
EX. 8	28	A-N,N-DIETHYL ACRYLAMIDE (N,N- DIETHYL- ACRYLAMIDE 5%MOL)	90	3	2.5	5 OR LESS
EX. 9	17	A-N,N-DIMETHYL- AMINOPROPYL ACRYLAMIDE (N,N- DIMETHYLAMINO- PROPYLACRYLAMIDE 5%MOL)	90	3	1.3	--
EX.10	17	A-N-VINYL- PYROLIDONE (N- VINYL PYROLIDONE 5%MOL)	80	3	2.5	-

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TABLE 1 (continued)

	ACROLEIN DENSITY (%WT)	CARBOXYLIC-ACID- BASED RESIN (COPOLYMER)	TEMP. (°C)	TIME (HR)	1,3-PROPANE -DIOL (%WT)	AMOUNT OF Pb (%WT)
EX.11	28	A-N-VINYL- PYROLIDONE (N- VINYL PYROLIDONE 5% MOL)	80	3	2.5	—
COMPARATIVE EX. 1	17	ION EXCHANGE RESIN	70	3	—	At 5 OR LESS
A represents acrylic acid						

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TABLE 2

	CONVERSION OF ACROLEIN (%)	SELECTIVITY OF 3-HYDROXYPROPANAL (%)	SELECTIVITY OF DIMERIZED 3-HYDROXYPROPANAL (%)	SELECTIVITY OF HYDROXYALKANAL (%)
EX. 1	44	57	9	66
EX. 2	51	77	15	92
EX. 3	38	64	23	87
EX. 4	56	67	12	79
EX. 5	41	60	20	80
EX. 6	42	57	19	76
EX. 7	46	57	18	75
EX. 8	58	65	12	77
EX. 9	30	64	16	80
EX. 10	28	71	8	79
EX. 11	17	65	9	74
COMPARATIVE EX. 1	44	46	5	51

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[0075] TABLE 2, reveals that using a carboxylic-acid-based resin having a nitrogen containing group as a catalyst can increase the reaction rate by heating while curbing the consecutive reaction of the reaction product, namely, 3-hydroxypropanal. Thus, 3-hydroxypropanal can be produced at high selectivity and yield out of a high-density acrolein solution. In addition, the catalyst retains excellent heat resistance and can be used repetitively.

[TWELFTH EXAMPLE]

[0076] A predetermined amount of water is poured into a reaction vessel equipped with a thermometer, a stirring instrument, and the like, and a predetermined amount of acrolein is also poured into the reaction vessel, so that the density of the resulting solution is 17 percent by weight. Also, a predetermined amount of lead-carrying ion exchange resin and 2.5 percent by weight of a carboxylic acid, namely, an oxalic acid, with respect to acrolein are added to the above solution. "Duolite" of Rohm & Haas Co., is used as the ion exchange resin, and an amount of lead carried by the resin is kept equal to or lower than a predetermined level, namely, not more than 5 percent by weight.

[0077] The above reaction solution is subject to reaction for two hours with stirring at 60°C to hydrate acrolein. When the reaction ends, the resulting reaction solution is filtered, and analyzed in a predetermined manner, the results of which are set forth below.

- (1) conversion of acrolein : 53%
- (2) selectivity of 3-hydroxypropanal : 85%
- (3) selectivity of dimerized 3-hydroxypropanal : 13%
- (4) selectivity of hydroxyalkanal : 98%
- (total of (3) and (4))

[THIRTEENTH EXAMPLE]

[0078] An analysis is conducted in the same manner as the twelfth example except that the density of acrolein is increased to 29 percent by weight from 17 percent by weight, and the reaction time is increased to three hours, the result of which are set forth below.

- (1) conversion of acrolein : 65%
- (2) selectivity of 3-hydroxypropanal : 40%
- (3) selectivity of dimerized 3-hydroxypropanal : 14%
- (4) selectivity of hydroxyalkanal : 54%
- (total of (3) and (4))

[SECOND COMPARATIVE EXAMPLE]

[0079] An analysis is conducted in the same manner as the twelfth-fifth example except that a carboxylic acid, namely, an oxalic acid, is omitted, the results of which are set forth below.

- (1) conversion of acrolein : 55%
- (2) selectivity of 3-hydroxypropanal : 79%
- (3) selectivity of dimerized 3-hydroxypropanal : 10%
- (4) selectivity of hydroxyalkanal : 89%
- (total of (3) and (4))

Here, the conversion of acrolein is low and an abundance of products are produced as a result of the consecutive reaction of 3-hydroxypropanal.

[0080] The results of the twelfth and thirteenth examples reveal that, when a catalyst is a lead-carrying ion exchange resin and an oxalic acid is added to the reaction solution, not only an industrially advantageous short-time conversion of acrolein can be improved, but also the consecutive reaction of the reaction product, namely, 3-hydroxypropanal, is curbed. Thus, 3-hydroxypropanal can be produced at high selectivity and yield out of a high-density acrolein solution.

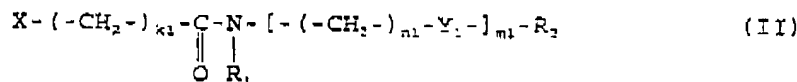
Claims

1. A process of producing a hydroxyalkanal comprising hydrating an unsaturated aldehyde of the general formula

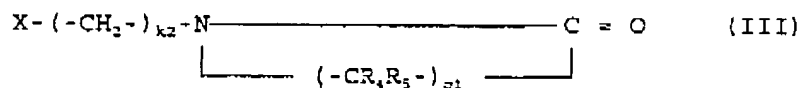
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in which R is a hydrogen atom or a hydrocarbon group having up to five carbon atoms, in solution in the presence of a carboxylic acid-based resin containing at least one substituent group selected from those of the general formulae



In which each of R_1 and R_2 is a hydrogen atom, a hydrocarbon group having up to five carbon atoms or $-(\text{CH}_2)_{p_1}-\text{X}$, each of p_1 , k_1 and m_1 is zero or an integer from one to six, n_1 is an integer from one to six, Y_1 is one of $-\text{O}-$, $-\text{S}-$ and $-\text{NR}_3-$, R_3 is a hydrogen atom or a hydrocarbon group having up to five carbon atoms and X represents the carboxylic acid-based resin main body;



In which each of R_4 and R_5 is a hydrogen atom or a hydrocarbon group having up to five carbon atoms, k_2 is zero or an integer from one to six, q_1 is an integer from three to six, and X represents the carboxylic acid-based resin main body;



in which R_6 is a hydrogen atom, a hydrocarbon group having up to five carbon atoms or $-(\text{CH}_2)_{p_2}-\text{X}$, p_2 is zero or an integer from one to six, R_7 is a hydrocarbon group having up to five carbon atoms or $-(\text{CH}_2)_{p_3}-\text{X}$, each of p_3 and k_3 is zero or an integer from one to six, and X represents the carboxylic acid-based resin main body, and wherein the ratio of carboxyl groups to nitrogen containing groups in the carboxylic acid-based resin ranges from 1/1000 to 1/1.

2. A process according to claim 1 in which the carboxylic acid-based resin is a copolymer of an unsaturated monomer (A) containing a carboxyl group and an unsaturated monomer (B) containing an amino group or both an amino and an amide group.
3. A process according to claim 2, wherein the nitrogen atom of the amino group and/or amide group of the unsaturated monomer (B) carries a substituent group of the general formula



In which n_3 is an integer from one to six, Y_3 is one of $-\text{O}-$, $-\text{S}-$, $-\text{NR}_{14}-$ and $-\text{CH}_2-$, R_{14} is a hydrogen atom or a hydrocarbon having up to five carbon atoms, m_3 is zero or an integer from one to six and R_{13} is a hydrogen atom, a hydrocarbon group having up to five carbon atoms or a Brønsted acid residue when $m_3 = 0$, or is a hydrogen atom or a hydrocarbon group having up to five carbon atoms when $m_3 \neq 0$.

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4. A process according to any one of claims 1 to 3, wherein the carboxylic acid-based resin carries at least one metal.
5. A process according to claim 4, wherein the metal is selected from copper, lead, nickel, zinc, iron, cobalt, bismuth, tin, antimony and alkaline earth metals.
6. A process according to claim 4 or claim 5, wherein the amount of metal carried by the carboxylic acid-based resin is from 0.001 to 10 percent by weight.
7. A process according to any one of claims 1 to 6, wherein the carboxylic acid-based resin is a (meth)acrylic acid-based resin.
8. A process according to claim 7, wherein the (meth)acrylic acid-based resin is selected from (meth)acrylic acid-(meth)acrylamide copolymers and (meth)acrylic acid-vinylpyrrolidone copolymers.
9. A process according to claim 1 in which the carboxylic acid based resin is a metal-carrying ion exchange resin.
10. A process according to claim 9, wherein an amount of metal carried by the ion exchange resin is from 0.001 to 10 percent by weight.
11. A process according to claim 10, wherein the metal is lead.
12. A process according to any one of claims 1 to 11, wherein hydration is carried out at a temperature from 50 to 250°C.
13. A process according to any one of claims 1 to 12, wherein hydration is carried out under a pressure from 0.1 to 2 MPa.
14. A process according to any one of claims 1 to 13, wherein the density of the unsaturated aldehyde solution is from 5 percent by weight to saturation.
15. A process according to any one of claims 1 to 14, wherein unsaturated aldehyde is selected from acrolein, methacrolein, 2-formyl-1-butene, 2-formyl-1-pentene, 2-formyl-1-hexene and 2-formyl-1-heptene.
16. A process according to claim 15, wherein the unsaturated aldehyde is acrolein and wherein hydration is carried out at a temperature from 50 to 140°C.
17. A process according to claim 16, carried out in the presence of 1,3-propanediol.
18. A process according claim 17, wherein the solution contains from 0.001 to 10 percent by weight 1,3-propanediol with respect to acrolein.
19. A catalyst for use in a process according to any one of claims 2 to 8 and 12 to 18, comprising a carboxylic acid-based resin of a copolymer of an unsaturated monomer (A) containing a carboxyl group with an unsaturated monomer (B) containing an amide group or both an amide and an amino group.
20. A catalyst according to claim 19, having the features specified in any one of claims 3 to 10.

Patentansprüche

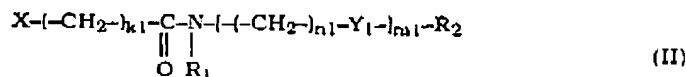
1. Verfahren zur Herstellung eines Hydroxyaldehyds, bei dem ein ungesättigter Aldehyd der allgemeinen Formel



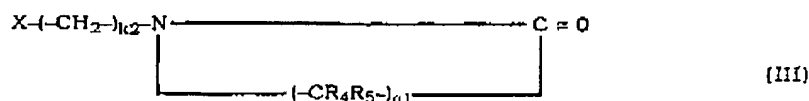
in der R für ein Wasserstoffatom oder eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen steht,

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In Lösung in Gegenwart eines Harzes auf Carbonsäurebasis hydratisiert wird, welches mindestens einen Substituenten ausgewählt aus solchen der allgemeinen Formeln



In der R_1 und R_2 jeweils für ein Wasserstoffatom, eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen oder $-(\text{CH}_2)_{p_1}-\text{X}$ stehen, P_1 , k_1 und m_1 jeweils für Null oder eine ganze Zahl von 1 bis 6, n_1 für eine ganze Zahl von 1 bis 6, Y_1 für $-\text{O}-$, $-\text{S}-$ oder $-\text{NR}_3-$, R_3 für ein Wasserstoffatom oder eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen und X für den Grundkörper des Harzes auf Carbonsäurebasis stehen,



In der R_4 und R_5 jeweils für ein Wasserstoffatom oder eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen, k_2 für Null oder eine ganze Zahl von 1 bis 6, q_1 für eine ganze Zahl von 3 bis 6 und X für den Grundkörper des Harzes auf Carbonsäurebasis stehen, und



In der R_6 für ein Wasserstoffatom, eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen oder $-(\text{CH}_2)_{p_2}-\text{X}$ steht, p_2 für Null oder eine ganze Zahl von 1 bis 6, R_7 für eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen oder $-(\text{CH}_2)_{p_3}-\text{X}$, p_3 und k_3 jeweils für Null oder eine ganze Zahl von 1 bis 6 und X für den Grundkörper des Harzes auf Carbonsäurebasis stehen, enthält, und wobei das Verhältnis von Carboxylgruppen zu Stickstoff enthaltenden Gruppen in dem Harz auf Carbonsäurebasis im Bereich von 1/1.000 bis 1/1 liegt.

2. Verfahren nach Anspruch 1, bei dem das Harz auf Carbonsäurebasis ein Copolymer eines ungesättigten Monomers (A), das eine Carboxylgruppe enthält, und eines ungesättigten Monomers (B), das eine Amidgruppe oder sowohl eine Aminogruppe als auch eine Amidgruppe enthält, ist.
3. Verfahren nach Anspruch 2, bei dem das Stickstoffatom der Aminogruppe und/oder der Amidgruppe des ungesättigten Monomers (B) einen Substituenten der allgemeinen Formel



trägt, in der n_3 für eine ganze Zahl von 1 bis 6, Y_3 für $-\text{O}-$, $-\text{S}-$, $-\text{NR}_{14}-$ oder $-\text{CH}_2-$, R_{14} für ein Wasserstoffatom oder eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen und m_3 für Null oder eine ganze Zahl von 1 bis 6 stehen und R_{13} für ein Wasserstoffatom, eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen oder einen Brønsted-Säurerest steht, wenn $m_3 \neq 0$ gilt bzw. für ein Wasserstoffatom oder eine Kohlenwasserstoffgruppe mit bis zu fünf Kohlenstoffatomen steht, wenn $m_3 = 0$ gilt.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem das Harz auf Carbonsäurebasis mindestens ein Metall trägt.

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5. Verfahren nach Anspruch 4, bei dem das Metall ausgewählt wird aus Kupfer, Blei, Nickel, Zink, Eisen, Kobalt, Bismuth, Zinn, Antimon und Erdalkalimetallen.
6. Verfahren nach Anspruch 4 oder Anspruch 5, bei dem die Menge an an dem Harz auf Carbonsäurebasis gebundenen Metall im Bereich von 0,001 bis 10 Gew.-% liegt.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem das Harz auf Carbonsäurebasis ein Harz auf (Meth-)Acrylsäurebasis ist.
8. Verfahren nach Anspruch 7, bei dem das Harz auf (Meth-)Acrylsäurebasis ausgewählt wird aus (Meth-)Acrylsäure-(Meth-)Acrylamid-Copolymeren und (Meth-)Acrylsäure-Vinylpyrrolidon-Copolymeren.
9. Verfahren nach Anspruch 1, bei dem das Harz auf Carbonsäurebasis ein metalltragendes Ionenaustauscherharz ist.
10. Verfahren nach Anspruch 9, bei dem die Menge an an dem Ionenaustauscherharz gebundenen Metall im Bereich von 0,001 bis 10 Gew.-% liegt.
11. Verfahren nach Anspruch 10, bei dem das Metall Blei ist.
12. Verfahren nach einem der Ansprüche 1 bis 11, bei dem die Hydratisierung bei einer Temperatur von 50 bis 250 °C durchgeführt wird.
13. Verfahren nach einem der Ansprüche 1 bis 12, bei dem die Hydratisierung unter einem Druck von 0,1 bis 2 MPa durchgeführt wird.
14. Verfahren nach einem der Ansprüche 1 bis 13, bei dem die Konzentration der Lösung des ungesättigten Aldehyds zwischen 5 Gew.-% und Sättigung liegt.
15. Verfahren nach einem der Ansprüche 1 bis 14, bei dem der ungesättigte Aldehyd ausgewählt wird aus Acrolein, Methacrolein, 2-Formylbut-1-en, 2-Formylpent-1-en, 2-Formylhex-1-en und 2-Formylhept-1-en.
16. Verfahren nach Anspruch 15, bei dem der ungesättigte Aldehyd Acrolein ist und bei dem die Hydratisierung bei einer Temperatur von 50 bis 140 °C durchgeführt wird.
17. Verfahren nach Anspruch 16, das in Gegenwart von Propan-1,3-diol ausgeführt wird.
18. Verfahren nach Anspruch 17, bei dem die Lösung bezogen auf das Acrolein 0,001 bis 10 Gew.-% Propan-1,3-diol enthält.
19. Katalysator zur Verwendung in einem Verfahren nach einem der Ansprüche 2 bis 8 und 12 bis 18, der mindestens ein Harz auf Carbonsäurebasis eines Copolymers eines ungesättigten Monomers (A), das eine Carboxylgruppe enthält, mit einem ungesättigten Monomer (B), das eine Amidgruppe oder sowohl eine Amidgruppe als auch eine Aminogruppe enthält, umfasst.
20. Katalysator nach Anspruch 19, der die in einem der Ansprüche 3 bis 10 angegebenen Merkmale besitzt.

Revendications

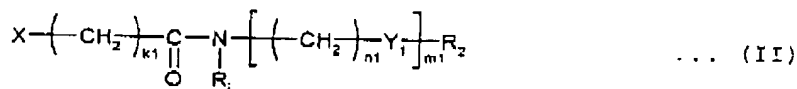
1. Procédé de production d'hydroxycanal, comprenant l'hydratation d'un aldéhyde insaturé de formule générale :



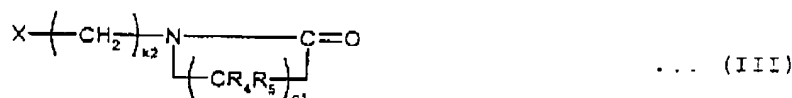
dans laquelle R représente un atome d'hydrogène ou un groupe hydrocarboné ayant jusqu'à 5 atomes de

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carbone, en solution en présence d'une résine à base d'acide carboxylique, contenant au moins un groupe de substitution choisi parmi ceux de formules générales :



où chacun de R_1 et R_2 est un atome d'hydrogène, un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone ou $-(\text{CH}_2)_{p_1}-\text{X}$, chacun de p_1 , k_1 et m_1 vaut zéro ou est un entier de 1 à 6, n_1 est un entier de 1 à 6, Y_1 est l'un de $-\text{O}-$, $-\text{S}-$ et $-\text{NR}_3-$, R_3 est un atome d'hydrogène ou un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone, et X représente le corps principal de la résine à base d'acide carboxylique ;



où chacun de R_4 et R_5 est un atome d'hydrogène ou un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone, k_2 vaut 0 ou est un entier de 1 à 6, q_1 est un entier de 3 à 6, et X représente le corps principal de la résine à base d'acide carboxylique ;



où R_6 est un atome d'hydrogène, un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone, ou $-(\text{CH}_2)_{p_2}-\text{X}$, p_2 vaut 0 ou est un entier de 1 à 6, R_7 est un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone ou $-(\text{CH}_2)_{p_3}-\text{X}$, chacun de p_3 et k_3 vaut 0 ou est un entier de 1 à 6, et X représente le corps principal de la résine à base d'acide carboxylique,

le rapport des groupes carboxyle aux groupes azotés dans la résine à base d'acide carboxylique étant situé dans la plage allant de 1/1000 à 1/1.

2. Procédé selon la revendication 1, dans lequel la résine à base d'acide carboxylique est un copolymère d'un monomère insaturé (A) contenant un groupe carboxyle et d'un monomère insaturé (B) contenant un groupe amide ou tant un groupe amino qu'un groupe amide.
3. Procédé selon la revendication 2, dans lequel l'atome d'azote du groupe amino et/ou du groupe amide du monomère insaturé (B) porte un groupe substituant de formule générale :



dans laquelle n_3 est un entier de 1 à 6, Y_3 est l'un de $-\text{O}-$, $-\text{S}-$, $-\text{NR}_{14}-$ et $-\text{CH}_2-$, R_{14} est un atome d'hydrogène ou un hydrocarbure ayant jusqu'à 5 atomes de carbone, m_3 vaut 0 ou est un entier de 1 à 6, et R_{13} est un atome d'hydrogène, un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone ou un résidu d'acide de Brønsted quand $m_3 \neq 0$, ou bien est un atome d'hydrogène ou un groupe hydrocarboné ayant jusqu'à 5 atomes de carbone quand $m_3 = 0$.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la résine à base d'acide carboxylique comporte au moins un métal.

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5. Procédé selon la revendication 4, dans lequel le métal est choisi parmi le cuivre, le plomb, le nickel, le zinc, le fer, le cobalt, le bismuth, l'étain, l'antimoine et les métaux alcalino-terreux.
- 5 6. Procédé selon la revendication 4 ou la revendication 5, dans lequel la quantité de métal présente dans la résine à base d'acide carboxylique est de 0,001 à 10 % en poids.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la résine à base d'acide carboxylique est une résine à base d'acide (méth)acrylique.
- 10 8. Procédé selon la revendication 7, dans lequel la résine à base d'acide (méth)acrylique est choisie parmi les copolymères acide (méth)acrylique/(méth)acrylamide et les copolymères acide (méth)acrylique/vinylpyrrolidone.
9. Procédé selon la revendication 1, dans lequel la résine à base d'acide carboxylique est une résine échangeuse d'ions comportant un métal.
- 15 10. Procédé selon la revendication 9, dans lequel la quantité de métal présente dans la résine échangeuse d'ions est de 0,001 à 10 % en poids.
11. Procédé selon la revendication 10, dans lequel le métal est le plomb.
- 20 12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel l'hydratation est réalisée à une température de 50 à 250°C.
13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel l'hydratation est réalisée sous une pression de 0,1 à 2 MPa.
- 25 14. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel la concentration de la solution d'aldéhyde insaturé va de 5 % en poids à la saturation.
15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel l'aldéhyde insaturé est choisi parmi l'acroléine, la méthacroléine, le 2-formyl-1-butène, le 2-formyl-1-pentène, le 2-formyl-1-hexène et le 2-formyl-1-heptène.
- 30 16. Procédé selon la revendication 15, dans lequel l'aldéhyde insaturé est l'acroléine et l'hydratation est réalisée à une température de 50 à 140°C.
17. Procédé selon la revendication 16, réalisé en présence de 1,3-propanediol.
18. Procédé selon la revendication 17, dans lequel la solution contient de 0,001 à 10 % en poids de 1,3-propanediol par rapport à l'acroléine.
- 40 19. Catalyseur à utiliser dans un procédé selon l'une quelconque des revendications 2 à 8 et 12 à 18, comprenant une résine à base d'acide carboxylique en un copolymère d'un monomère insaturé (A) contenant un groupe carboxyle et d'un monomère insaturé (B) contenant un groupe amide ou tant un groupe amide qu'un groupe amino.
- 45 20. Catalyseur selon la revendication 19, ayant les caractéristiques spécifiées dans l'une quelconque des revendications 3 à 10.
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